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THERMOCHEMISTRY OF GASEOUS COMPOUNDS OF METALS.(U)
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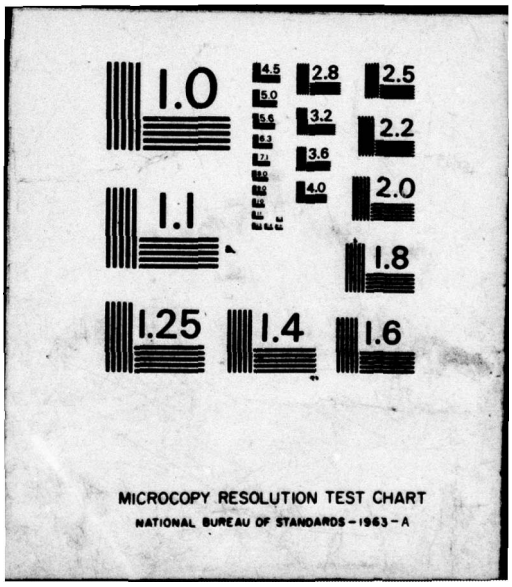
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(10) Prepared by
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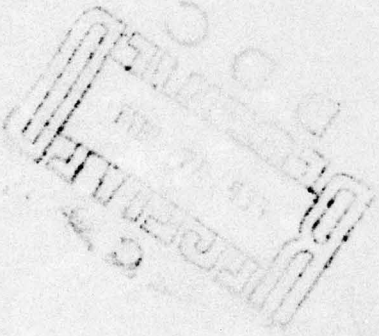

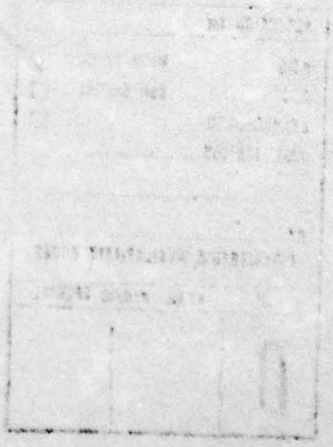

ABSTRACT

Thermochemical studies of a number of gaseous metal halides and oxides have been carried out by high temperature mass spectrometry, including CaI, SrI, BaI, EuF, EuF_2 and SmO. Dissociation energies and heats of formation are derived from the data, and the results are compared with the predictions of several theoretical models where possible. For the IIA metal iodides, the experimental dissociation energies follow trends established by the fluorides, chlorides and bromides; the results are compatible with corrected Birge-Sponer extrapolations and with electrostatic model calculations. The data for D_0°(BaI) suggest that chemiluminescent spectra resulting from the Ba + I_2 reaction may be due in part to the reaction of electronically-excited Ba atoms. Sublimation data for CaI_2(s), and vaporization data for $SrI_2(\ell)$ and $BaI_2(\ell)$ obtained by the torsion-effusion method are consistent with estimated molecular parameters of the gaseous diiodide molecules, leading to accurate thermochemical data for these molecules. The results for SmO, in addition to providing an accurate value of D_0°(SmO), resolve a long-standing discrepancy between the dissociation energies of SmO and EuO. And finally, torsion-effusion studies of the dissociative vaporization of PbF_2(s) yielded new thermochemical data for PbF_4(g).

INTRODUCTION

From a knowledge of the thermodynamics of chemical reactions, one can draw certain conclusions about the deposition of energy in the reaction products and about the equilibrium distribution of products as well. Both of these applications are important in the development of Air Force technology. Recently, much interest has been focused on the study of elementary metal oxidation reactions as possible pumping steps

in the development of chemical lasers operating in the visible or UV. Halogens as well as oxygen are used as oxidant. The thermochemistry of many of the metal-oxidant systems of interest, however, is not sufficiently well characterized for an adequate evaluation of the chemical energy release. Furthermore, spectroscopic studies of these chemiluminescent metal oxidation processes have been interpreted to yield reaction energies which are sometimes in serious disagreement with established or estimated thermochemical data. To aid in resolving these conflicts and to provide a sound data base for the development of modeling schemes to fill in the inevitable gaps, the studies described herein were undertaken. During this past year, the effort was devoted to completing studies of the Ca, Sr, and Ba iodides and to beginning work on some of the lanthanide oxides and halides.

RESULTS AND DISCUSSION

(a) IIA Iodides

Isomolecular exchange reactions involving CaI, SrI, and BaI were studied by mass spectrometry, using AlI and GaI as reference molecules. Beams containing the molecules of interest were generated by the reaction of gaseous HI with mixtures of the IIA oxides and Ga_2O_3(s) or Al_2O_3(s); a little AlB_{12}(s) was added to increase the Al activity. Derived isomolecular equilibrium constants were found to be independent of the HI flow rate, demonstrating equilibrium behavior. BaI was measured with respect to GaI rather than AlI because of unresolved overlap of AlI^+ and BaO^+ at nominal m/e 154. The results are summarized in Table 1; agreement between second and third law heats is considered satisfactory. Dissociation energies of the monoiodides were derived

by reference to AlI (D_0° = 85.0 ± 2 kcal/mol) and GaI (D_0° = 82.0 ± 1 kcal/mol). A second value for SrI was derived by reference to SrI_2 via reaction 3.

Results of the effusion vaporization studies on the Ca, Sr, and Ba diiodides are summarized in Table 2. These measurements were made with alumina effusion cells, at temperatures substantially lower than the measurements of Peterson and Hutchison[1] reviewed in the JANAF Tables. Thermodynamic data obtained from our vaporization studies are in close agreement with the JANAF derived quantities, and thus corroborate the molecular constant assignments of the diiodides.

In Table 3 are given the standard enthalpies of formation and dissociation energies of the gaseous metal iodides obtained from our studies. The two different results for SrI derived by reference to AlI and SrI_2 agreed to within 0.3 kcal/mol. In similar fashion, the present result for BaI from reaction 4 agrees closely with the value $D_0^\circ(BaI)$ = 71.2 kcal/mol reported previously from studies of the gaseous reaction Ba + BaI_2 = 2 BaI. As seen in Table 4, the thermochemical dissociation energies of the monoiodides are in good agreement with the predictions of the Rittner electrostatic model, and with ionicity-corrected Birge-Sponer extrapolations (LBX); however, uncertainties in the equilibrium internuclear distances lead to a moderate spread in the calculated values. Thermochemical data for the Ca, Sr, and Ba monohalides are now complete; the results clearly establish trends in the binding energies that can be used reliably to evaluate the missing values for the bromides and iodides of beryllium and magnesium. A comparison of our result for BaI with the value D_0°(BaI) = 102 ± 1 kcal/mol from chemiluminescent reaction studies[2] indicates clearly that the interpretation of the chemiluminescent measurements is incorrect. In fact, it now appears that the chemiluminescent spectra were strongly influenced by the presence of metastable

barium atoms in the oven beam. Thus the thermochemical data make a valuable contribution by helping to uncover systematic errors in the analysis of the chemiluminescence data. This is important in that the chemiluminescent reaction technique is a promising new approach for determining molecular energy quantities.

(b) Europium Fluorides

Gaseous europium fluorides were studied by mass spectrometry using a double chamber beam source in which $CaF_2(g)$ passed over $Eu_2O_3(s)$. EuF and EuF_2 were identified in the equilibrium beam along with Ca and CaF, permitting reactions 5 and 6 to be studied. The results are given in Table 1. Since the electronic partition functions of EuF and EuF_2 are uncertain, thermochemical results are based solely on second law analysis; parent ion abundance measurements were made by pulse counting techniques. Derived thermochemical quantities are given in Table 3. Zmbov and Margrave[3] reported $D_0^\circ(EuF) = 125.3 \pm 4$ kcal/mol, in fair agreement with our value, but no experimental data have been reported previously for $EuF_2(g)$. In this instance, the value $D_0^\circ(EuF) \geq 129.6 \pm 2.1$ kcal/mol obtained from chemiluminescent reaction spectroscopy[4] seems compatible with our thermochemical result. The estimates $D_0^\circ(EuF_2) = 262.5 \pm 11$ kcal/mol and $\Delta Hf_{298}^\circ(EuF_2,g) = -160 \pm 10$ kcal/mol have been made.[3] In contrast to the wide variations observed in other metal halides, the two bond dissociation energies D(Eu-F) and D(FEu-F) appear to be almost identical. Because of the low first ionization potentials of the lanthanide metals, the metal halides should be highly ionic and therefore susceptible to an electrostatic model calculation. A preliminary ionic model calculation gives $D_0^\circ(EuF) = 126$ kcal/mol, in fair agreement with the experimental value. Further application of the ionic model to the

lanthanide halides will be explored, particularly where internuclear distances are known accurately (HoF, TbF, LuF, YbF).

(c) Samarium Monoxide

Isomolecular exchange reactions of SmO with AlO, TiO, and EuO were studied by mass spectrometry, with the results summarized in Table 1. Extensive second law measurements of the SmO-AlO exchange reaction were made by both pulse counting and dc methods, in order to check the calculated free energy functions of SmO. The AlO and TiO results are quite concordant, leading to the derived thermochemical quantities in Table 3. Our derived $D_0^\circ(SmO)$ is somewhat lower than the value 142.0 ± 4.6 reported by Ames et al.,[5] but is again compatible with the chemiluminescent reaction result ≥ 135.5 ± 0.7 kcal/mol. Data for the SmO-EuO exchange reaction are entirely consistent with the new value $D_0^\circ(EuO)$ = 111.9 ± 2.4 kcal/mol,[6] but differ sharply with previous mass spectrometric studies of this exchange reaction which yielded $[D_0^\circ(SmO - D_0^\circ(EuO)]$ = 13.0 ± 1.9 kcal/mol.[5] It is concluded that the earlier measurements on the SmO-EuO reaction[5] contain a large systematic error, of presently unknown origin. In any event, the new data resolve the previous discrepancies and firmly establish the dissociation energies of SmO and EuO.

(d) Lead Fluorides

In order to check the chemical energy release in the chemiluminescent fluorination of lead atoms, the available thermochemical data for the Pb-F system were examined. Previous mass spectrometric investigation[6] of the vaporization of PbF_2 in the range 1040 to 1160 K indicated disproportionation to Pb(ℓ) and PbF_4(g) as the dominant process. There were no direct measurements of the absolute pressure in this range, although the derived JANAF data lead to PbF_4 pressures of 10^{-3} atm or

higher, beyond the normal molecular effusion regime. Therefore, the vaporization of $PbF_2(s)$ was reinvestigated by the torsion-effusion method over the range 748-812 K using a graphite effusion cell. Highly reproducible pressures were obtained, along with vapor molecular weights indicating the vapor to be predominantly PbF_4. Results are summarized in Table II. Pressures of $PbF_2(g)$ and Pb(g) calculated from JANAF Table data are more than an order of magnitude lower than the observed pressures. Second and third law results for the PbF_4 disproportionation reaction are in close agreement, and are in good accord with the JANAF selected values $\Delta H_{298} = 52.2 \pm 5.1$ kcal/mol and $\Delta Hf^{\circ}_{298}(PbF_4, g) = -270.9 \pm 5$ kcal/mol.

PERSONNEL

Personnel contributing to the project, in addition to the principal investigator, were Drs. K. H. Lau and P. D. Kleinschmidt, Postdoctoral Fellows.

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Table 1

SUMMARY OF DERIVED THERMODYNAMIC DATA FOR GASEOUS REACTIONS

	Reaction	Data Points	Range, K	ΔH_T (II) kcal/mol	ΔH_{298} (II) kcal/mol	ΔH_{298} (III) kcal/mol
(1)	Ca + AlI = CaI + Al	10	1541-1674	23.1 ± 3.0	22.9	23.2
(2)	Sr + AlI = SrI + Al	13	1626-1810	24.8 ± 1.7	24.5	22.1
(3)	Sr + SrI_2 = 2 SrI	10	1626-1787	-	-	26.9
(4)	Ba + GaI = BaI + Ga	14	1711-1886	9.4 ± 1.6	9.3	10.5
(5)	Eu + CaF = EuF + Ca	11	1878-2013	-2.7 ± 2.3	-2.7	-
(6)	EuF + CaF = EuF_2 + Ca	12	1824-2013	-2.5 ± 1.7	-3.9	-
(7)	Al + SmO = AlO + Sm	19	2087-2298	13.1 ± 1.3	13.1	13.3
		25	2110-2295	11.9 ± 0.8	11.9	13.0
(8)	Sm + TiO = Sm + TiO	6	2120-2242	-	-	22.2
(9)	Eu + SmO = EuO + Sm	6	2120-2242	-	-	24.8

II = second law.
III = third law.

Table 2

SUMMARY OF METAL HALIDE VAPORIZATION DATA

Vaporization Process	Data Points	Range, K	ΔS_T (II) cal/mol	ΔH_T (II) kcal/mol	ΔH_{298} (II) kcal/mol	ΔH_{298} (III) kcal/mol
$CaI_2(s) = CaI_2(g)$	14	970-1035	39.0 ± 0.2	64.2 ± 0.2	68.0	66.4
$SrI_2(\ell) = SrI_2(g)$	9	958-1003	27.7 ± 0.5	57.2 ± 0.5	63.6	65.8
$BaI_2(\ell) = BaI_2(g)$	8	985-1051	32.3 ± 0.8	64.1 ± 0.8	70.6	67.9
$2PbF_2(s,\beta) = Pb(\ell) + PbF_4(g)$	13	748-812	29.5 ± 0.2	45.3 ± 0.2	52.6	52.8

II = second law.

III = third law.

Table 3

DERIVED THERMOCHEMICAL DATA*

Gaseous Molecule	ΔHf°_{298} kcal/mol	D°_{0} kcal/mol
CaI	5.5	62.1
SrI	0.6	63.6
BaI	-3.8	71.6
CaI_2	-61.9	155.1
SrI_2	-65.4	155.1
BaI_2	-72.1	165.3
EuF	-68.9	128.9
EuF_2	-180.9	259.0
SmO	-28.0	136.0
PbF_4	-270.3	389.6

*Preliminary estimated uncertainty ± 2 kcal/mol.

Table 4

COMPARISON AT D_0°(MI) VALUES, kcal/mol

	This Work	Ionic Model	LBX (corr)
CaI	62.1 ± 2	59	70
SrI	63.6 ± 2	62	59
BaI	71.6 ± 2	67	70

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